Mixing of atomic states and the shape of ionic spectral lines in a plasma

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We use the atomic density matrix formalism to investigate how the shape of an emission line is affected by the population dynamics of the radiating atomic states, and also to discuss the problem of lifetimes of metastable levels. The special case of a three-level system is investigated in detail. Our results show that spectral line shapes in a plasma cannot be treated properly unless we simultaneously account for changes in both the spectral function and the populations of the radiating atomic levels.

1. INTRODUCTION

The traditional theory of spectral line broadening is based on calculating the spectral functions for the radiating atomic states, while assuming that the populations of these states are prespecified and treating their calculation as a separate problem in atomic kinetics. Although calculations that include simultaneous variability of atomic populations and spectral functions have been carried out for problems in nonlinear spectroscopy,[1] these calculations only treat interactions with a quasimonochromatic (laser) field. The calculations of the broadening of atomic spectral lines due to collisions in a dense plasma described in Ref. 2 simultaneously included the evolution of populations and polarization within the framework of a static approximation; similar calculations in Ref. 3 were based on numerical multi-frequency simulation of the ion dynamics. In this paper we will calculate the influence of mixing of atomic states on the shape of atomic spectral lines in the approximation of binary (pairwise) collisions; this approximation allows us to evaluate the contribution of these effects in explicit analytic form, both for the static and collisional portions of the line shape.

Note that the problem of mixing of atomic states is closely related to problems of radiation and decay during atomic collisions (see Refs. 4–9), and in particular to the problem of calculating the lifetime of metastable levels[4,5] and the generation of forbidden spectral line components.[6–9]

Actually, loss of metastability during a collision is a by-product of radiative deexcitation of the atomic systems in the course of a collision, i.e., it accompanies the generation of spectral line intensities that are specifically due to collisions. When these intensities are integrated over the spectrum, they give rise to a nontrivial dependence of the radiative deexcitation cross section on the radiative decay rate Γ, as noted in Refs. 4, 5. In what follows, we investigate not only the integral of the line shape but also the spectral characteristics associated with the possibility of radiation during collisions.

Radiative deexcitation effects can make themselves felt during collisions under the following two conditions: when the value of the decay constant Γ is rather large, a characteristic, e.g., of states of multicharged ions,[2,3] and when the duration of the collisions is long, a characteristic of collisions involving long-range interactions (dipole–charge) in a dense plasma.[2,3]

With regard to general theoretical principles, the present paper is a generalization of the classic theory of Griem, Barange, Kolb, and Ortel[9] to the case of states with large radiative decay constants, i.e., states that are characteristic of multiply-charged ions. It also generalizes the theory of generation of forbidden atomic emission line components in a plasma to include ionic emission lines.[6–9] In line with this formulation of the problem, we discuss the simplest three-level scheme for atomic states (Fig. 1), in which level 2 decays to the lower state 1 with a rate Γ by an allowed dipole transition, whereas the decay $3\rightarrow 1$ is assumed to be dipole forbidden (levels 2 and 3 are separated in energy by an interval ω_{32}). This scheme leads to formulations both of the problem of metastable state lifetimes[4,5] and that of generation of forbidden components of spectral lines.[6–9] For both the allowed I_a $(2\rightarrow 1)$ and forbidden I_f $(3\rightarrow 1)$ transitions, the cause of radiative deexcitation and line broadening is pairwise collisions between the aforementioned radiating ion (atom) and a second atom that causes the broadening; this atom (ion) is assumed to have a charge Z_i, and (for simplicity) to move along a straight-line trajectory $r^2(t)=\rho^2+(z-vt)^2$ with impact parameter ρ and velocity v. The condition that the collisions be pairwise (binary) corresponds to

$$N\rho_{\text{eff}}^3 \ll 1, \tag{1.1}$$

where N is the ion density and ρ_{eff} the effective radius of the collisions that cause the broadening or radiative deexcitation.

Thus, the density dependence of the line shape under discussion is trivial (proportional to N), and the primary problem consists of calculating its dependence on velocity and relaxation constant.

2. GENERAL EQUATIONS. ADIABATIC APPROXIMATION

The starting equations, which take into account the evolution of both populations and polarization, are the equations for the atomic density matrix $\hat{\rho}$ (Refs. 1–3):

$$\frac{d\hat{\rho}}{dt}+\hat{\Gamma}\hat{\rho}=[\hat{\rho},\hat{H}_0+\hat{V}+\hat{V}_\mu]+\hat{\Phi}\hat{\rho}+Q, \tag{2.1}$$

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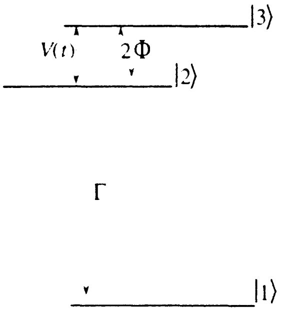

FIG. 1. Diagram of the levels used in the calculation of the emission line shape.

where $\hat{\Gamma}$ is the relaxation matrix, $\hat{\Phi}$ is the matrix for collisional mixing of states by electrons, $\hat{H}_0$ is the Hamiltonian of a free atom, Q is the collisional pumping,

$$V(t)=\alpha/[\rho^2+(z-vt)^2] \tag{2.2}$$

is the interaction of the atom with the field of the perturbing ion, which is characterized by the interaction constant α (where $\alpha=\langle 2|d_z|3\rangle$),

$$V_\mu(t)=G\exp(-i\omega t) \tag{2.3}$$

is the interaction of an atom with a mode of the spontaneous radiation field characterized by the observed frequency ω and interaction constant G, whose square is related to the radiative decay rate Γ, see Ref. 1.

The solution to (2.1) is constructed as usual according to perturbation theory in the quantity G, so that $\hat{\rho}=\hat{\rho}^0+\hat{\rho}^\mu$, where $\hat{\rho}^0$ determines the evolution of the populations and $\hat{\rho}^\mu$ (for brevity denoted simply by $\hat{\rho}$) the evolution of the polarization.

In the zeroth approximation we obtain for the matrix ρ^0 the equations (see Ref. 2)

$$\begin{aligned}
\dot{\rho}^0_{22}&=-\Gamma\rho^0_{22}-iV_{23}\rho^0_{32}+iV_{32}\rho^0_{23}+2\Phi(\rho^0_{33}-\rho^0_{22})+Q_2,\\
\dot{\rho}^0_{33}&=iV_{23}\rho^0_{32}-iV_{32}\rho^0_{23}-2\Phi(\rho^0_{33}-\rho^0_{22})+Q_3,\\
\dot{\rho}^0_{32}&=-(\Gamma/2-i\omega_{32})\rho^0_{32}+iV_{32}(\rho^0_{33}-\rho^0_{22}),\\
\rho^0_{23}&=(\rho^0_{32})^*.
\end{aligned} \tag{2.4}$$

For the polarization matrix $\hat{\rho}$ we have to first order in G

$$\begin{aligned}
\dot{\rho}_{21}&=-(i\omega_{21}+\Gamma/2+\Phi)\rho_{21}-iV_{23}\rho_{31}\\
&\quad+i\rho^0_{22}G\exp(-i\omega t),\\
\dot{\rho}_{31}&=-(i\omega_{31}+\Phi)\rho_{31}-iV_{32}\rho_{21}\\
&\quad+i\rho^0_{32}G\exp(-i\omega t),
\end{aligned} \tag{2.5}$$

where $\omega_{ij}=\omega_i-\omega_j$ ($i, j=1, 2, 3$).

The perturbation $V(t)$ in Eqs. (2.4), (2.5) we will assume to be slowly varying in time (adiabatic) in the sense that

$$\rho_{\rm eff}\omega_{32}/v\gg 1. \tag{2.6}$$

Condition (2.6) is the basis for constructing an adiabatic theory of broadening analogous to that used in Ref. 8. Within the framework of this condition it is still possible to separate the lineshape into quasistatic ($\rho_{\rm eff}|\Delta\omega|/v\gg 1$) and collisional ($\rho_{\rm eff}|\Delta\omega|/v\ll 1$) broadening regions (in this notation, $\Delta\omega_{31}=\omega-\omega_{31}$, $\Delta\omega_{21}=\omega_{21}-\omega$ are offsets from resonance).

Even when condition (2.6) is used, the general solution to this system (2.4), (2.5) is still too cumbersome. Therefore, we consider the solution in two ranges of the variables.

When $\max\{\Gamma\rho_{\rm eff}V^2/\omega_{32}^2 v,\Gamma\rho_{\rm eff}/v\}\gg 1$, the system may be considered adiabatic not only with respect to the spacing ω_{32}, but also with respect to the effective decay rate in the collision process, i.e., $\max\{\Gamma V^2/\omega_{32}^2,\Gamma\}$. In this ("doubly" adiabatic) case the solution to system (2.4) has the form

$$\begin{pmatrix}\rho^0_{22}\\ \rho^0_{33}\end{pmatrix}=\int_{-\infty}^{t}d\tau\hat{S}(t,\tau)\begin{pmatrix}Q_2\\ Q_3\end{pmatrix}, \tag{2.7}$$

where the evolution operator $\hat{S}(t,\tau)$ is

$$\hat{S}(t,\tau)=[1-a_1(\tau)b_2(\tau)]^{-1}\times\begin{pmatrix}-a_1(t)b_2(\tau)\exp\left(\int_\tau^t\lambda_1dt\right)+\exp\left(\int_\tau^t\lambda_2dt\right)a_1(t)\exp\left(\int_\tau^t\lambda_1dt\right)-a_1(\tau)\exp\left(\int_\tau^t\lambda_2dt\right)\\ -b_2(\tau)b_2(t)\exp\left(\int_\tau^t\lambda_1dt\right)+b_2(t)\exp\left(\int_\tau^t\lambda_2dt\right)-a_1(\tau)b_2(t)\exp\left(\int_\tau^t\lambda_2dt\right)+\exp\left(\int_\tau^t\lambda_1dt\right)\end{pmatrix}. \tag{2.8}$$

Here we have introduced the notation

$$\begin{aligned}
a_1(t)&=\left[\frac{\Gamma V^2(t)}{\omega_{32}^2}+2\Phi\right]\left[\frac{\Gamma}{2}+\sqrt{\frac{\Gamma^2}{4}+\left(2\Phi+\frac{\Gamma V^2(t)}{\omega_{32}^2}\right)^2}\right]^{-1},\\
b_2(t)&=-\left[-\frac{\Gamma}{2}+\sqrt{\frac{\Gamma^2}{4}+\left(2\Phi+\frac{\Gamma V^2(t)}{\omega_{32}^2}\right)^2}\right]\times\left[\frac{\Gamma V^2(t)}{\omega_{32}^2}+2\Phi\right]^{-1},\\
\lambda_{1,2}(t)&=-\frac{\Gamma}{2}-2\Phi-\frac{\Gamma V^2(t)}{\omega_{32}^2}\pm\sqrt{\frac{\Gamma^2}{4}+\left(2\Phi+\frac{\Gamma V^2(t)}{\omega_{32}^2}\right)^2}.
\end{aligned} \tag{2.9}$$

The off-diagonal element of the density matrix ρ^0_{32} is

$$\rho^0_{32}=V(t)[\rho^0_{33}(t)-\rho^0_{22}(t)]/(\omega_{32}+i\Gamma/2). \tag{2.10}$$

In the opposite limiting case $\max\{\Gamma\rho_{\rm eff}V^2/\omega^2_{32}v,\Gamma\rho_{\rm eff}/v\}\ll 1$, relaxation during the collision can be neglected, and the solution of the system (2.4) has the form

$$\rho^0_{22}=\frac{Q_2+Q_3}{\Gamma}+\frac{Q_3}{2\Phi}\frac{2V^2(t)}{\omega^2_{32}+4V^2(t)},$$

$$\rho^0_{33}=\frac{Q_2+Q_3}{\Gamma}+\frac{Q_3}{2\Phi}-\frac{Q_3}{2\Phi}\frac{2V^2(t)}{\omega^2_{32}+4V^2(t)}, \tag{2.11}$$

$$\rho^0_{32}=\frac{Q_3}{2\Phi}\frac{V\omega_{32}}{\omega^2_{32}+4V^2}.$$

The solution to the polarization equations (2.5) in the adiabatic limit (2.6) can be written in the form

$$\begin{aligned}\rho_{21}(t)=i\int_{-\infty}^{t}dt_1[1+a^2(t_1)]^{-1}\Big\{[\rho^0_{22}(t_1)\\ -a(t_1)\rho^0_{32}(t_1)]\exp\Big[-i\omega t_1-i\omega_{21}(t-t_1)\\ +i\int_{t_1}^{t}d\tau\kappa(\tau)-(\Gamma/2+\Phi)(t-t_1)\\ +\int_{t_1}^{t}d\tau\gamma(\tau)\Big]+[a(t)\rho^0_{32}(t_1)\\ +a(t)a(t_1)\rho^0_{22}(t_1)]\exp\Big[-i\omega t_1-i(\omega_{31}\\ -i\Phi)(t-t_1)-i\int_{t_1}^{t}d\tau\kappa(\tau)\\ -\int_{t_1}^{t}d\tau\gamma(\tau)\Big]\Big\},\end{aligned} \tag{2.12}$$

where we have introduced the notation

$$\kappa=(\sqrt{\omega^2_{32}+4V^2}-\omega_{32})/2,$$

$$\gamma=(\Gamma/4)(1-\omega_{32}/\sqrt{\omega^2_{32}+4V^2}), \tag{2.13}$$

$$a=2V/(\sqrt{\omega^2_{32}+4V^2}+\omega_{32}).$$

The spectrum of emitted power in the vicinity of the transition $2\to 1$ ($\omega_{32}\ll\omega$) is calculated by evaluating the work done by the probe field G according to the expression in Ref. 1:

$$P(\omega)=-2\omega_{21}\,\mathrm{Re}\langle iG^*\exp(i\omega t)\rho_{21}\rangle. \tag{2.14}$$

In what follows we will be interested in both the total probability of radiative deexcitation of the metastable state 3 (integrated over ω) and the frequency distribution of radiatively deexcited power (i.e., the shapes of the allowed and forbidden spectral lines).

3. LIFETIME OF METASTABLE STATES DUE TO RADIATIVE DEEXCITATION DURING A COLLISION

The problem of finding the lifetime τ of metastable levels of atoms and ions in a plasma is a classic problem with applications to astrophysics and plasma physics.[4,5,10–13] Here we will be interested in the lifetime τ arising from slow adiabatic collisions during which the metastable state 3 has the option of radiating (i.e., radiative deexcitation) due to its mixing with the radiating state 2. This problem was investigated in Refs. 4, 5 within the framework of an amplitude approach. Here we will find corresponding results by using the density matrix method, and refine some of the results of the calculations in Ref. 4.

Let us consider the system (2.4). It has a steady-state solution in the absence of collisions, due to the pumping Q and relaxations Γ, Φ. Let us separate this solution from the general one and consider only those solutions $\Delta\rho^0$ that arise from collisions. In light of what was said above, we represent the matrix ρ^0 in the form

$$\begin{aligned}\rho^0_{22}&=\Delta\rho^0_{22}+(Q_2+Q_3)/\Gamma,\\ \rho^0_{33}&=\Delta\rho^0_{33}+(Q_2+Q_3)/\Gamma+Q_3/2\Phi.\end{aligned} \tag{3.1}$$

Substituting (3.1) into (2.4) we find

$$\begin{aligned}\dot\rho^0_{22}&=-\Gamma\Delta\rho^0_{22}-iV_{23}\rho^0_{32}+iV_{32}\rho^0_{23}\\ &\quad+2\Phi(\Delta\rho^0_{33}-\Delta\rho^0_{22}),\\ \dot\rho^0_{33}&=iV_{23}\rho^0_{32}-iV_{32}\rho^0_{23}-2\Phi(\Delta\rho^0_{33}-\Delta\rho^0_{22}),\\ \dot\rho^0_{32}&=-(\Gamma/2-i\omega_{32})\rho^0_{32}-iV_{32}(\Delta\rho^0_{33}-\Delta\rho^0_{22})\\ &\quad+iV_{32}Q_3/2\Phi.\end{aligned} \tag{3.2}$$

As we have already noted, the general solution (3.2) is quite complicated. Therefore, we limit ourselves, as before, to calculating its solutions in two limiting cases: small and large effective decay constants Γ. In the first case we may neglect the decay Γ within a collision time $\rho_{\rm eff}/v$, and the corresponding results for $\Delta\rho$ follow from solving (2.11), so that

$$\begin{aligned}\Delta\rho^0_{22}(t)&=\frac{Q_3}{2\Phi}\frac{2V^2(t)}{\omega^2_{32}+4V^2(t)},\\ \Delta\rho^0_{33}(t)&=-\frac{Q_3}{2\Phi}\frac{2V^2(t)}{\omega^2_{32}+4V^2(t)}.\end{aligned} \tag{3.3}$$

In the second case the decay during the collisions is significant ($\Gamma\rho_{\rm eff}/v\gg 1$) and we must use the general solution (2.8)–(2.10). However, it is important to take the decay into account only for distant collisions, which possess long durations (large $\rho_{\rm eff}$). For these the effective value of the perturbation $V(t)$ is small ($V_{\rm eff}\ll\omega_{32}$), so that we may use an expansion of the evolution operator $S(t,\tau)$. This leads to the following result for $\Delta\rho$:

$$\Delta\rho^0_{22}(t)=\frac{Q_3}{2\Phi}\frac{V^2(t)}{\omega^2_{32}}\exp\Big[-\frac{\Gamma}{2}\int_{-\infty}^{t}d\tau\frac{V^2(\tau)}{\omega^2_{32}}\Big]. \tag{3.4}$$

It is easy to verify using (2.12) that the integrated radiative probability I (with respect to ω) of interest is

$$I=\int_{-\infty}^{\infty} d\omega P(\omega)=\Gamma\omega_{21}\langle\Delta\rho_{22}^{0}(t)\rangle, \tag{3.5}$$

where the symbol $\langle...\rangle$ denotes averaging over an ensemble of perturbing particles (see (2.2)):

$$\langle...\rangle=2\pi N\int_{0}^{\infty} d\rho\rho\int_{-\infty}^{\infty} dz(...). \tag{3.6}$$

It is obvious that averaging with respect to $dz=vdt$ eliminates the time dependence in (3.5).

Further calculation of the quantity I requires the use of the limiting expressions (3.4), (3.5). In this case it is convenient to divide the corresponding expressions by the steady-state population $Q_3/2\Phi$, and to use Eq. (3.6) to introduce effective radiative deexcitation cross sections, which are determined by integrals over ρ. As a result, for $\Gamma\rho_{\rm eff}/v=\xi\ll 1$ (where $\rho_{\rm eff}=\sqrt{\alpha/\omega_{32}}$) we obtain

$$\sigma=2\pi\int_{0}^{\infty} d\rho\rho\int_{-\infty}^{\infty} dt\frac{2\Gamma V^2(t)}{\omega_{32}^2+4V^2(t)}$$

$$=\pi^2\sqrt{2}\frac{\Gamma}{v}\left(\frac{\alpha}{\omega_{32}}\right)^{3/2}\equiv\sigma_{ad}. \tag{3.7}$$

In the opposite limiting case $\xi\gg 1$, using (3.4) we likewise obtain

$$\sigma=2\pi\int_{0}^{\infty} d\rho\rho\int_{-\infty}^{\infty} dt\frac{\Gamma V^2(t)}{2\omega_{32}^2}$$

$$\times\exp\left[-\int_{-\infty}^{t} d\tau\frac{\Gamma V^2(\tau)}{2\omega_{32}^2}\right], \tag{3.8}$$

where after carrying out the integration with respect to t and substituting in the explicit form of $V(t)$ we get

$$\sigma=\pi^{5/3}\Gamma(1/3)(\Gamma/2)^{2/3}\alpha^{4/3}v^{-2/3}\omega_{32}^{-4/3}\equiv\sigma_{\rm W}. \tag{3.9}$$

Here the symbol $\sigma_{\rm W}$ corresponds to the "Weisskopf" cross section determined in Refs. 4, 5.

A detailed comparison of the results (3.7), (3.9) with the data of Ref. 4 shows that the Weisskopf cross section (3.9) coincides in accuracy with that derived in Ref. 4. At the same time, for the case of the adiabatic cross section (3.7) our numerical coefficient differs from the analogous coefficient in Ref. 4. Analysis shows that the difference is related to the approximate choice of coefficients made in Ref. 4 when treating the amplitude of the metastable state. Incidentally, the numerical difference of the two coefficients is negligible in this limit (less than 10%).

Thus, the method we have developed not only reproduces the results of Ref. 4 obtained earlier, which are based on the amplitude approach, but in the general case refines them. Let us now turn to calculating the spectral dependences of the radiated power.

4. CALCULATION OF THE SPECTRUM. SHAPES OF THE ALLOWED AND FORBIDDEN LINES

The general expression (2.12) describes the polarization for a radiative transition to state 1 from a system of two nearby mixed levels 2 and 3, described by the matrix $\rho^0(t)$. In the present case of densities that are not too high ($N\rho_{\rm eff}^3\ll 1$), the spectrum of this system consists of two pronounced maxima near the allowed component (with a frequency offset of $\Delta\omega_{21}$) and forbidden component (with a frequency offset of $\Delta\omega_{31}$). Therefore, we will investigate them separately. Let us first consider the normalized line shape $J(\omega)$:

$$J(\omega)=-{\rm Re}\langle iG^*\exp(i\omega t)\rho_{21}(t)\rangle/\pi|G|^2\langle\rho_{22}^0(t)\rangle. \tag{4.1}$$

We begin the discussion by examining the shape $J_a(\Delta\omega_{21})$ of the allowed line, which according to (2.12) has the following form:

$$J_a(\Delta\omega_{21})=\frac{1}{\pi\langle\rho_{22}^0\rangle}{\rm Re}\left\langle\int_{-\infty}^{t} dt_1\frac{\rho_{22}^0(t_1)-a(t_1)\rho_{32}^0(t_1)}{1+a^2(t_1)}\right.$$

$$\times\exp\left[-i\omega t_1-i\omega_{21}(t-t_1)+i\int_{t_1}^{t} d\tau\kappa(\tau)\right.$$

$$\left.\left.-\left(\frac{\Gamma}{2}+\Phi\right)(t-t_1)+\int_{t_1}^{t} d\tau\gamma(\tau)\right]\right\rangle, \tag{4.2}$$

here the symbol $\langle...\rangle$ denotes averaging over the phase volume of all the broadening particles. In the approximation of binary collisions, this average can be reduced in the standard way to an average over the phase volume of a single particle using the so-called collisional volume $m(t)$ (see Ref. 8). For the cases discussed below, the use of this averaging is not critical. Nevertheless, in the interest of generality we will compute it.

In the present case of binary collisions, it is easy to verify that the character of the broadening is determined by a transition from a collisional region to a static region as we move away from the line center. This transition takes place entirely within the region of the quadratic Stark effect ($V_{\rm eff}\ll\omega_{32}$). A further transition to the region of the linear Stark effect ($V_{\rm eff}\gg\omega_{32}$) takes place even in the static portion of the spectrum.

Let us begin this discussion with the most interesting region (with regard to the transition from the collisional broadening mechanism to the static mechanism), i.e., that of the quadratic Stark effect $V\ll\omega_{32}$.

In the limit $\Gamma\rho_{\rm eff}/v\ll 1$, in which the decay during a collision is small, using for ρ^0 the result (2.11) when $V\ll\omega_{32}$ leads to

$$J_a=\frac{1}{\pi}\,\mathrm{Re}\int_{-\infty}^{t}dt_1\exp\left[-i\Delta\omega_{21}(t-t_1)-\left(\frac{\Gamma}{2}+\Phi\right)(t-t_1)\right.$$

$$\left.+Nm_1(t,t_1)\right]+\frac{N}{\pi}\frac{Q_3\Gamma}{(Q_2+Q_3)2\Phi}$$

$$\times\mathrm{Re}\int_{-\infty}^{t}dt_1\,\frac{2V^2(t_1)-V(t)V(t_1)}{\omega_{32}^2}$$

$$\times\exp\left[-i\Delta\omega_{21}(t-t_1)+i\int_{t_1}^{t}d\tau\kappa(\tau)\right.$$

$$\left.-\left(\frac{\Gamma}{2}+\Phi\right)(t-t_1)+\int_{t_1}^{t}d\tau\gamma(\tau)+Nm_1(t,t_1)\right].\qquad(4.3)$$

Here $m_1(t,t_1)$ is the collisional volume:

$$m_1(t,t_1)=2\pi\int_0^\infty\rho d\rho\int_{-\infty}^{\infty}dz\left\{1-\exp\left[i\int_{t_1}^{t}d\tau(\kappa(\tau)\right.\right.$$

$$\left.\left.-i\gamma(\tau))\right]\right\}.\qquad(4.4)$$

Equation (4.3) contains three terms. The first of these describes a standard binary line shape for the allowed component, broadened by relaxation and collisions. The second term describes a contribution from the forbidden component to the shape of the allowed component due to the pumping Q_3. This contribution is entirely due to mixing of forbidden and allowed states in the course of the broadening collision.

From (4.3) it is easy to obtain an expression for the line shape both in the collisional region ($\rho_W|\Delta\omega_{21}|/v\ll1$) and in the static region ($\rho_W|\Delta\omega_{21}|/v\gg1$) (where ρ_W is the Weisskopf radius, which determines the cross section of the broadening collision for the case of the quadratic Stark effect). Thus, in the collisional regime ($|\Delta\omega_{21}|\ll\Omega_W\equiv v/\rho_W$) we obtain

$$J_a\cong\frac{1}{\pi}\frac{\gamma/2}{(\Delta\omega_{21}-\Delta)^2+\gamma^2/4}$$

$$-\frac{Q_3\Gamma}{(Q_2+Q_3)2\Phi}N\frac{\pi}{2}\frac{\alpha^2}{v\omega_{32}^2}\ln\left(\frac{\rho_{\max}}{\rho_{\min}}\right),\qquad(4.5)$$

where Δ,γ are the collisional adiabatic shift and broadening of the allowed line.

In the static region ($\Delta\omega_{21}\gg\Omega_W$) we have

$$J_a\cong N\pi\alpha^{3/2}\left(\frac{1}{(\Delta\omega_{21})^{7/4}\omega_{32}^{3/4}}\right.$$

$$\left.+\frac{Q_3\Gamma}{(Q_2+Q_3)2\Phi}\frac{1}{(\Delta\omega_{21})^{3/4}\omega_{32}^{7/4}}\right).\qquad(4.6)$$

From (4.5), (4.6) it is clear that the standard profile of the allowed line is changed in both the collisional and static regions, due to contributions caused by the pumping Q_3 at the forbidden transition and by state 3 "mixing into" the allowed state 2 because of this pumping. In this case even the spectral dependence of the wings of the static contour are changed, as is clear from (4.6) [$(\Delta\omega_{21})^{-3/4}$ instead of $(\Delta\omega_{21})^{-7/4}$]. However, this change is characteristic only of the spectral offsets $\Delta\omega_{21}\ll\omega_{32}$ that correspond to the region of the quadratic Stark effect. Nevertheless, according to (4.5), (4.6) the contour of the allowed line $J_a(\Delta\omega_{21})$ undergoes a considerable change: the intensity in the collisional region decreases, and there is an increase in the static wing of the line.

In the limit $\Gamma\rho_{\text{eff}}/v\gg1$, which corresponds to a large decay constant Γ, it is necessary to include in the matrix ρ^0 the possibility of decay during the collision; see (3.4). Then from (4.2) we obtain

$$J_a=\frac{1}{\pi}\,\mathrm{Re}\int_{-\infty}^{t}dt_1\exp\left\{-i\Delta\omega_{21}(t-t_1)-\left(\frac{\Gamma}{2}+\Phi\right)(t-t_1)\right.$$

$$\left.+N[m_1(t,t_1)+m_\Gamma(t,t_1)]\right\}+\frac{N}{\pi}\frac{Q_3\Gamma}{(Q_2+Q_3)2\Phi}$$

$$\times\mathrm{Re}\int_{-\infty}^{t}dt_1\,\frac{V^2(t_1)-V(t)V(t_1)}{\omega_{32}^2}\exp\left[-i\Delta\omega_{21}(t\right.$$

$$-t_1)+i\int_{t_1}^{t}d\tau\kappa(\tau)-\left(\frac{\Gamma}{2}+\Phi\right)(t-t_1)+\int_{t_1}^{t}d\tau\gamma(\tau)$$

$$\left.+N[m_1(t,t_1)+m_\Gamma(t,t_1))\right]-\Gamma\int_{-\infty}^{t_1}\frac{d\tau V^2(\tau)}{\omega_{32}^2}],$$

(4.7)

where we have introduced the collisional volume $m_\Gamma(t,t_1)$ related to the decay (compare with Ref. 4):

$$m_\Gamma(t,t_1)=2\pi\int_0^\infty\rho d\rho\int_{-\infty}^{\infty}dz\left\{1-\exp\right.$$

$$\left.\times\left[-\int_{t_1}^{t}d\tau\frac{\Gamma V^2(\tau)}{2\omega_{32}^2}\right]\right\}.$$

Estimating the integrals in (4.7) for large Γ, we find

$$J_a\cong\frac{1}{\pi}\frac{\Gamma/2}{\Delta\omega_{21}^2+\Gamma^2/4}+\frac{N\pi\alpha^{3/2}}{\omega_{32}^2(\Delta\omega_{21}^2+\Gamma^2/4)^{7/8}},\qquad(4.8)$$

i.e., for large Γ the line shape consists of a Lorentz contour for spontaneous emission and the usual static contour (proportional to $(\Delta\omega_{21})^{-7/4}$) for large $\Delta\omega$.

Let us now calculate the line shape in the region of the linear Stark effect, which corresponds to the distant wings ($\Delta\omega_{21}\gg\omega_{32}$). In this case we separate the Lorentz contour for spontaneous broadening caused by the decay rate Γ from the contour caused by collisions. Let us write $\rho_{22}^0(t)$ in the form

$$\rho_{22}^0(t)=\langle\rho_{22}^0(t)\rangle+\Delta\rho_{22}^0(t).$$

By integrating the term in (4.2) with $\langle\rho_{22}^0(t)\rangle$ by parts and retaining only terms proportional to the density N, we find

$$J_a \cong \frac{1}{\pi} \frac{\Gamma/2}{\Delta\omega_{21}^2+\Gamma^2/4} - N\frac{1}{\pi}\mathrm{Re}\int_{-\infty}^{t} dt_1 \frac{i\kappa(t_1)}{i\Delta\omega_{21}+(\Gamma/2+\Phi)}$$

$$\times\exp\left[-i\Delta\omega_{21}(t-t_1)+i\int_{t_1}^{t} d\tau\kappa(\tau) - \left(\frac{\Gamma}{2}+\Phi\right)(t-t_1)+\int_{t_1}^{t} d\tau\gamma(\tau)\right]$$

$$+\frac{N}{\pi\langle\rho_{22}^0\rangle}\mathrm{Re}\int_{-\infty}^{t} dt_1\left[\Delta\rho_{22}^0(t_1) - \frac{a^2(t_1)}{1+a^2(t_1)}\rho_{22}^0(t_1) - \frac{\rho_{32}^0(t_1)a^2(t_1)}{1+a^2(t_1)}\right]\exp\left[-i\Delta\omega_{21}(t-t_1)+i\int_{t_1}^{t} d\tau\kappa(\tau) - \left(\frac{\Gamma}{2}+\Phi\right)(t-t_1) + \int_{t_1}^{t} d\tau\gamma(\tau)\right]. \qquad (4.9)$$

The integrals in (4.9) in the region under discussion, i.e., static broadening, are calculated by the method of stationary phase. When $\Gamma\alpha^{1/2}(\Delta\omega_{21})^{3/2}/v\omega_{32}^2 \gg 1$ we obtain

$$J_a \cong \frac{\pi N \alpha^{3/2}(\Delta\omega_{21}+\omega_{32})}{[\Delta\omega_{21}(\Delta\omega_{21}+\omega_{32})]^{7/4}} \times\left[1-\frac{\Delta\omega_{21}}{\omega_{32}}\frac{\Gamma Q_3/(Q_2+Q_3)}{\Gamma\Delta\omega_{21}(\Delta\omega_{21}+\omega_{32})/\omega_{32}^2+2\Phi}\right]. \qquad (4.10)$$

For $\Gamma\alpha^{1/2}(\Delta\omega_{21})^{3/2}/v\omega_{32}^2 \ll 1$ we have

$$J_a \cong \frac{\pi N \alpha^{3/2}(\Delta\omega_{21}+\omega_{32})}{[\Delta\omega_{21}(\Delta\omega_{21}+\omega_{32})]^{7/4}} \times\left[1+\frac{Q_3\Gamma}{(Q_2+Q_3)2\Phi}\frac{2\Delta\omega_{21}(\Delta\omega_{21}+\omega_{32}/2)}{\omega_{32}^2+4\Delta\omega_{21}(\Delta\omega_{21}+\omega_{32})}\right]. \qquad (4.11)$$

This latter result reproduces Eq. (4.6) for $\Delta\omega_{21}\ll\omega_{32}$. However, in the region $\Delta\omega_{21}\gg\omega_{32}$, the falloff of the static line shape has its standard form, i.e., $J_a \propto (\Delta\omega_{21})^{-5/2}$. In this case, the role of mixing effects reduces to a simple redistribution of the populations caused by pumping at levels Q_2 and Q_3.

Let us now calculate the line shape $J_f(\Delta\omega_{31})$ near the forbidden line $3\to1$. From the general expression (2.12), after dividing by the normalization we obtain

$$J_f = \frac{1}{\pi\langle\rho_{22}^0\rangle}\mathrm{Re}\left\langle a(t)\int_{-\infty}^{t} dt_1 \frac{a(t_1)\rho_{22}^0(t_1)+\rho_{32}^0(t_1)}{1+a^2(t_1)} \times\exp\left[i\Delta\omega_{31}(t-t_1) - i\int_{t_1}^{t} d\tau\kappa(\tau) - \Phi(t-t_1) - \int_{t_1}^{t} d\tau\gamma(\tau)\right]\right\rangle. \qquad (4.12)$$

In the calculations that follow, we will omit the collision volumes, which are unimportant in the binary-collision regime under discussion here.

In the region where the quadratic Stark effect is important ($\Delta\omega_{31}\ll\omega_{32}$), by proceeding in the same way as we did for the allowed component, we obtain for large and small values of Γ

$$J_f(\Delta\omega_{31}) \cong \frac{2Nv}{\langle\rho_{22}^0\rangle}\mathrm{Re}\int_0^\infty \rho d\rho\int_{-\infty}^{\infty} dt\frac{V(t)}{\omega_{32}^2}\int_{-\infty}^{t} dt_1 \times V(t_1)\left\{\frac{Q_2}{\Gamma}+\frac{Q_3}{\Gamma}\exp\left[-\int_{-\infty}^{t_1} d\tau\frac{\Gamma V^2(\tau)}{2\omega_{32}^2}\right] + \frac{Q_3}{2\Phi}\exp\left[-\int_{-\infty}^{t_1} d\tau\frac{\Gamma V^2(\tau)}{2\omega_{32}^2}\right]\right\} \times\exp\left[i\Delta\omega_{31}(t-t_1) - i\int_{t_1}^{t} d\tau\kappa(\tau) - \Phi(t-t_1) - \int_{t_1}^{t} d\tau\gamma(\tau)\right], \quad \Gamma\rho_{\rm eff}/v \gg 1, \qquad (4.13)$$

$$J_f(\Delta\omega_{31}) \cong \frac{2Nv}{\langle\rho_{22}^0\rangle}\mathrm{Re}\int_0^\infty \rho d\rho\int_{-\infty}^{\infty} dt\frac{V(t)}{\omega_{32}^2}\int_{-\infty}^{t} dt_1 \times V(t_1)\left(\langle\rho_{22}^0\rangle+\frac{Q_3}{2\Phi}\right)\exp\left[i\Delta\omega_{31}(t-t_1) - i\int_{t_1}^{t} d\tau\kappa(\tau) - \Phi(t-t_1) - \int_{t_1}^{t} d\tau\gamma(\tau)\right],$$

$$\Gamma\rho_{\rm eff}/v \ll 1. \qquad (4.14)$$

In the collisional broadening region $|\Delta\omega_{31}|\ll\Omega_W$, we obtain from (4.13), (4.14)

$$J_f(\Delta\omega_{31}) \cong N\frac{\pi}{2}\frac{\alpha^2}{v\omega_{32}^2}\ln\left(\frac{\rho_{\max}}{\rho_{\min}}\right)\left[1+\frac{Q_3\Gamma}{(Q_2+Q_3)2\Phi}\right]. \qquad (4.15)$$

Comparing (4.15) with (4.5), we verify that the falloff in intensity of the allowed component is precisely compensated by the increase in intensity of the forbidden component.

In the static region $\Delta\omega_{31}\gg\Omega_W$, Eq. (4.13) contains both limiting cases (4.13) and (4.14). Using it in this limit to perform the necessary integrations by the saddle-point method, we likewise obtain

$$J_f(\Delta\omega_{31}) \cong N\frac{\pi\rho_\omega^2}{\langle\rho_{22}^0\rangle}\int_0^{\rho_\omega}\rho d\rho\frac{1}{\sqrt{\alpha/(\Delta\omega_{31})^{1/2}\omega_{32}^{1/2}-\rho^2}}\left[\frac{Q_2}{\Gamma} + Q_3\left(\frac{1}{\Gamma}+\frac{1}{2\Phi}\right)\exp\left(-\frac{\Gamma\pi\alpha^2}{4v\rho^3\omega_{32}^2}\right)\right], \qquad (4.16)$$

where $\rho_\omega=\alpha^{1/2}/(\omega_{32}\Delta\omega_{31})^{1/4}$.

In the limit $\Gamma\alpha^{1/2}(\Delta\omega_{31})^{3/4}/v\omega_{32}^{5/4}\ll 1$, we find from (4.16) that

$$J_f(\Delta\omega_{31}) \cong \frac{\pi N \alpha^{3/2}}{\omega_{32}^{7/4}(\Delta\omega_{31})^{3/4}} \left[1+\frac{Q_3\Gamma}{(Q_2+Q_3)2\Phi}\right], \quad (4.17)$$

while in the limit $\Gamma\alpha^{1/2}(\Delta\omega_{31})^{3/4}/v\omega_{32}^{5/4} \gg 1$,

$$J_f(\Delta\omega_{31}) \cong \frac{\pi N \alpha^{3/2}}{\omega_{32}^{7/4}(\Delta\omega_{31})^{3/4}} \frac{Q_3}{(Q_2+Q_3)}. \quad (4.18)$$

In the present case of $\Delta\omega_{31} \ll \omega_{32}$, this latter limit can be realized only when the inequality $\xi = \Gamma\sqrt{\alpha}/v\sqrt{\omega_{32}} \gg 1$ holds.

Thus, the characteristic falloff in the spectral dependence of the forbidden component in the region of the quadratic Stark effect is determined by the factor $(\Delta\omega_{31})^{-3/4}$. The expressions in front of this factor depend on the ratio between the pumps Q_2 and Q_3, and on the possibility that their populations could decay in the course of a broadening collision.

In the region of transition to the linear Stark effect $(\Delta\omega_{31} \gg \omega_{32})$, the effective impact parameter responsible for the broadening is $\rho_{\text{eff}} = \rho_\omega$. Accordingly, the results for small and large values of the parameter Γ have the form

$$J_f \cong \frac{\pi N \alpha^{3/2}\Delta\omega_{31}}{[\Delta\omega_{31}(\Delta\omega_{31}+\omega_{32})]^{7/4}} \left[1+\frac{Q_3\Gamma}{(Q_2+Q_3)2\Phi} \times \frac{2\Delta\omega_{31}(\Delta\omega_{31}+\omega_{32}}{\omega_{32}^2+4\Delta\omega_{31}(\Delta\omega_{31}+\omega_{32})}\right],$$
$$\Gamma\alpha^2/v\rho_\omega^3\omega^2 \ll 1, \quad (4.19)$$

$$J_f \cong \frac{\pi N \alpha^{3/2}\Delta\omega_{31}}{[\Delta\omega_{31}(\Delta\omega_{31}+\omega_{32})]^{7/4}} \left[1+\frac{\Delta\omega_{31}+\omega_{32}}{\omega_{32}} \times \frac{\Gamma Q_3/(Q_2+Q_3)}{\Gamma\Delta\omega_{31}(\Delta\omega_{31}+\omega_{32})/\omega_{32}^2+2\Phi}\right],$$
$$\Gamma\alpha^2/v\rho_\omega^3\omega_{32}^2 \gg 1. \quad (4.20)$$

Comparing these expressions with (4.9), (4.10), we verify that they coincide precisely in structure with the factors that determine mixing for the allowed component.

The limiting cases we have discussed above exhaust the possible regions of spectral functions for the allowed and forbidden components.

5. CONCLUSION

The basic conclusions of the investigation we have carried out can be summarized as follows:

1. The shape of a line depends not only on the spectral function but also on the relation between the pump and relaxation parameters of the radiating levels. This reveals new possibilities for diagnostics of the populations of excited atomic states in a plasma based on studying the line shapes.
2. One of the most striking effects of the mixing of states is the possibility of abruptly increasing the intensity in the wings of the allowed and forbidden lines [see (4.6), (4.11), (4.17), (4.19)].
3. The mixing of states during a broadening collision leads to a redistribution of intensity among the various components of the spectral line, in particular, among the allowed and forbidden components in the collisional region, which corresponds to maximum intensity [see (4.5), (4.15)].

Let us assess the possibility of observing the effects we have computed here. According to our discussion in this paper, this possibility is contingent on the magnitudes of two basic parameters: the ratio of the radiative and collisional line widths $\Gamma/2\Phi$, and the probability of decay during the collision process $\Gamma^2\alpha/\omega v^2$. We should expect a deviation from the results of the standard theory of broadening at large values of the first parameter (where radiative decays predominate) and small values of the second parameter (steady-state populations cannot be set up during a collision). Furthermore, the conditions for pairwise collisions and adiabaticity should be satisfied.

For hydrogenic ions, all of the conditions listed above are satisfied with regard to order of magnitude under the conditions of the experiments[5]; however, the corresponding threshold values are found to be at the edge of applicability of these conditions. For the conditions discussed in Ref. 3, the conditions for applicability of our approximations are satisfied for the broadening of Ar–H^+ pairs at densities $N_e \leq 10^{22}$ cm^{-3}, which exhibits a sudden growth in intensity of the wings of the line as is qualitatively predicted by our calculations. The largest effects should be expected when we go to heavier elements.

For forbidden transitions in helium-like ions, the situation as a whole is analogous. The most radical changes in the spectrum should be expected when heavy ions are broadened by light ones; for ionic charges greater than 25, and for comparatively small electron densities $N_e \leq 10^{22}$ cm^{-3}, we should expect changes in the intensity of several orders of magnitude.

Evidence for these effects can be found not only in the spectra of multiply-charged ions, but also in the spectra of neutral hydrogen under astrophysical conditions corresponding to the plasma parameters investigated in Ref. 14. Here, despite the smallness of the fine-structure intervals that separate the individual sublevels of the hydrogen atom, the temperature of the broadening ions is on the one hand low enough that a portion of the broadening collisions will be adiabatic, and on the other hand high enough that steady-state populations cannot be established in the levels.

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